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1087.054

## PATENT SPECIFICATION

NO DRAWINGS

1087.054



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## COMPLETE SPECIFICATION

## Tinning of Aluminium

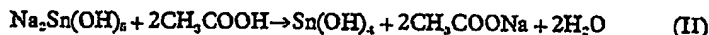
- We, M & T CHEMICALS INC., a corporation organized and existing under the State of Delaware, United States of America, of 100 Park Avenue, New York, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to a process for immersion plating of aluminium, including aluminium alloys, with tin and to compositions used in making up these baths.

Tin may be plated on aluminium by immersing aluminium in aqueous baths containing an alkali metal stannate. These baths may be operated over a wide temperature range from room temperature to about 90° C., at pH typically higher than 12.5, to produce a tin deposit which may vary in colour from gray to white, and may have a matte appearance. Tin may deposit from the bath in accordance with Equation (I).



- The deposition of tin releases free hydroxide, and the amount of free hydroxide formed per square foot of aluminium treated may depend on such factors as temperature, concentration of the various bath components, and immersion time. It has been found that the thickness of the tin layer deposited on aluminium by this process and the rate of deposition thereof increases at an undesirably high rate with increase of free alkali content. It is desirable to be able to control the thickness and rate of deposit and to operate the process so that the resulting coating meets a specified minimum thickness, but does not exceed a predetermined maximum thickness.

Prior art techniques have attempted to remedy the build-up of free hydroxide and control it within operative limits by the addition of acids such as acetic acid. Unfortunately it is not possible to readily control this reaction and over-neutralization (particularly at the point of introduction of the acid) occurs, even when using dilute acid. The local excess of acetic acid may react immediately with the alkali metal stannate to precipitate tin as the hydroxide in the form of a sludge, typically according to Reaction (II) which illustrates a reaction which may occur when acetic acid is used to neutralize the free hydroxide.



- The stannic hydroxide sludge, once formed, may be substantially impossible to redissolve during normal operation of the immersion tinning bath and represents lost tin. A loss of tin (of as much as 25% of the tin present) in the form of sludge is not uncommon and this depletion considerably decreases the life of the bath. Furthermore, sludge particles in the bath may adhere to the surface of the work result-

ing in an unsatisfactory surface finish. Often the baths are prematurely discarded, since sludge may build up to such an extent that making up a new solution may be more economical than trying to rectify the old one.

In attempts to minimize problems resulting from the use of acetic acid neutralization of excess free hydroxide, other compounds have been used in the bath to neutralize the free

hydroxide as it is formed; but the inclusion of such compounds has not heretofore reduced the amounts of acid required. However because of the absence of any satisfactory techniques for solving the problem, acetic acid is commonly employed, the addition being accompanied by vigorous agitation.

It is an object of this invention to provide an improved process for the immersion tinning of aluminium which in this Specification includes aluminium alloys. It is a further object of this invention to provide aqueous alkali metal stannate baths useful for the immersion tinning of aluminium. It is another object of this invention to provide compositions useful for making up and maintaining aqueous alkali metal stannate baths.

In accordance with one aspect of this invention, the method of this invention for treating aluminium to form a surface layer of tin therein comprises immersing the aluminium in an aqueous bath comprising a nitrogen-containing Jongkind-chelating agent, and sodium stannate or potassium stannate, maintaining the aluminium in the bath for time sufficient to deposit a surface layer of tin thereon, and withdrawing the aluminium from the bath.

The said nitrogen-containing Jongkind-chelating agent may be chosen from ethylene diamine tetraacetic acid, N,N-dihydroxy ethyl glycine, and water-soluble salts thereof.

The aluminium which is treated by the practice of this invention preferably is commercially pure aluminium or an alloy of aluminium. Typical of such alloys are those containing copper, magnesium, or both copper and magnesium. One of the more common aluminium alloys which can be treated by the process of this invention may contain 2%—4%, say 3% copper, 1%—1.5%, say 1.5% magnesium, 9%—13%, say 10% silicon, and quantities of other metals such as zinc, iron and nickel. Such alloys are commonly used for the fabrication of aluminium pistons. A specific illustration of one of these alloys may be that identified as Permanent Mold Casting Alloy D-132 containing 3% copper, 1% magnesium, 10% silicon, 0.5% manganese, 0.5% zinc, and the remainder aluminium.

The immersion baths which may be used in practice of this invention are typically made up by dissolving potassium stannate and/or sodium stannate in water to form a bath containing from 15 g/l (grams per litre) to saturation, typically 70 g/l of the stannate salt, the resulting solution containing 30 g/l of tin. Sufficient potassium hydroxide and/or sodium hydroxide may be initially added to form a bath containing 4 g/l of the metal hydroxide to prevent precipitation of tin due to low pH during makeup. During operation, the free alkali metal hydroxide may be maintained between 0.5 g/l to 12 g/l, preferably between 1 g/l and 8 g/l, say 4 g/l. Proper operation of

the bath may normally be carried out at a pH sufficiently high to keep the stannate in solution. Since tin may precipitate from these baths at pH below about 11.5, normal operation of these baths may be at pH above this point and preferably at pH of at least 12. This pH may normally be maintained automatically by the hydroxide generated and it may not normally be necessary to add hydroxide to the baths.

In accordance with this invention there is added to the solution a nitrogen-containing Jongkind-chelating agent. A nitrogen-containing Jongkind-chelating agent is a nitrogen-containing chelating agent which is characterized by the ability to complex or chelate at least one metal chosen from copper in solutions containing at least 1.2 Normal hydroxide ion, and magnesium in solutions containing at least 0.7 Normal hydroxide ion, the chelating ability being present when the agent is present in amount of one and one-half moles per mole of copper or magnesium metal present.

Specifically to determine whether or not a nitrogen-containing chelating agent is a nitrogen-containing Jongkind-chelating agent, the following procedure is followed:

(a) Prepare a first standard solution by dissolving one millimole of copper sulfate in 10 ml of distilled water. 1.5 millimoles of the chelating agent to be tested is added to the solution and the volume made up with distilled water to 35 ml. To this solution there is added from a burette 2 normal aqueous potassium hydroxide solution, slowly with stirring. The volume of potassium hydroxide solution is noted when a permanent precipitate forms (i.e. one which does not redissolve on stirring). A nitrogen-containing Jongkind chelating agent which passes this first or copper chelating test is one which does not permit formation of a permanent precipitate on addition of 50 ml of the 2 normal aqueous potassium hydroxide solution.

(b) Prepare a second standard solution in manner identical to the first except that one millimole of magnesium sulfate is substituted for the one millimole of copper sulfate. The remainder of this test procedure is identical to that using the copper sulfate. A nitrogen-containing Jongkind chelating agent which passes this second or magnesium-chelating test is one which does not permit formation of a permanent precipitate on addition of 20 ml of the 2 normal aqueous potassium hydroxide solution.

Although a nitrogen-containing Jongkind-chelating agent is an agent which passes either portion of this test, it is found that outstanding results may be obtained when the agent passes both portions of the test.

In a preferred embodiment, the nitrogen-containing Jongkind-chelating agent is chosen from ethylene diamine tetraacetic acid (i.e. versene (Trade Mark) or EDTA); water-

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soluble salts of this compound, commonly designated as "versenates", (Trade Mark) typically alkali metal salts such as the disodium salt of ethylene diamine tetraacetate; the monosodium salt of N,N-dihydroxy ethyl glycine, the trisodium salt of N-hydroxy ethyl ethylene diamine triacetic acid.

The nitrogen-containing Jongkind-chelating agent is added, preferably with agitation, to the aqueous stannate bath independently or jointly with the stannates which are used to make up and also to maintain the baths.

Preferably, the nitrogen-containing Jongkind-chelating agent may be employed in an amount of 0.01 mole to 0.25 mole, say 0.1 mole/l. Smaller amounts may be employed, but they do not substantially control the thickness of the immersion plate or the formation of sludge. Greater amounts may be employed but no substantial additional improvement may be obtained thereby.

Immersion plating in accordance with this invention may be carried out between room temperature of e.g. 20° C. and 90° C., and preferably between 40° C. and 80° C., say 60° C. Immersion time may be as little as 30 seconds, but it is usually between 1—6 minutes, e.g. 4 minutes. During this time, the aluminium will be coated with a layer of tin of desired thickness.

For make up and maintenance of the baths, preferred compositions contain 80%—99% by weight of potassium stannate and/or sodium stannate and 1%—20% of at least one compound comprising the nitrogen-containing Jongkind-chelating agent. Preferred compositions contain 90%—98% of the stannate and 10%—2% of at least one nitrogen-containing Jongkind-chelating agent. An illustrative composition comprises 98% potassium stannate and 2% disodium salt of ethylene diamine tetraacetic acid. The compositions containing lower percentage of the agent e.g. 2%—5% may be used for replenishment or maintenance while the compositions with the higher agent content e.g. 5%—20% may be used for the make up of new baths. Illustrative of these are the following compositions:

1. potassium stannate	96%
disodium salt of ethylene diamine tetraacetic acid	4%
2. sodium stannate	97%
disodium salt of ethylene diamine tetraacetic acid	3%

3. potassium stannate	99%	55
tetrasodium salt of ethylene diamine tetraacetic acid	1%	
4. sodium stannate	86%	
tetrasodium salt of ethylene diamine tetraacetic acid	14%	60
5. potassium stannate	98%	
monosodium salt of N,N-dihydroxy ethyl glycine	2%	
6. sodium stannate	97%	65
monosodium salt of N,N-dihydroxy ethyl glycine	3%	

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative and comparative Examples are given:

#### EXAMPLE 1.

Four solutions were made up containing 70 g/l of potassium stannate each and respectively 2, 4, 8 and 12 g/l of potassium hydroxide. The solutions were held at a temperature of 60° C. In each of the solutions, one of four identical discs of piston aluminium alloy (D—132) was immersed for exactly 4 minutes during which time a layer of tin was deposited on the disc.

The discs were removed from the solution, dried, and weighed. Then the tin deposit was stripped from the disc by immersion in a mixture of 3 parts of water and one part of concentrated nitric acid and the discs weighed again. From the loss of weight, the thickness of the coating was calculated.

Then to each of the solutions monosodium salt of N,N-dihydroxy ethyl glycine was added, the immersion tinning process was repeated, and the plating thickness determined as before. Successively at intervals, additional aliquots of monosodium salt of N,N-dihydroxy ethyl glycine were added, until each of the four solutions contained 20 g/l of the said glycine salt; and after each addition, the plating thickness obtained by use of the solution was determined.

The above procedure was in a similar fashion repeated for trisodium salt of N-hydroxyethyl ethylene diamine tetraacetic acid and disodium salt of ethylene diamine tetraacetic acid in place of the said glycine salt. By way of comparison the above procedure was repeated but without using any nitrogen-containing Jongkind-chelating agent. The results are shown in Table I.

TABLE I

Additive	KOH Concentration g/l							
	g/l	1.5	2	4	6	8	9	12
	(tin thickness in millionths of an inch)							
none	—	—	92	105	—	205	207	239
Monosodium salt of N,N-dihydroxy ethyl glycine	20	—	74	104	—	158	—	151
Trisodium salt of N-hydroxyethyl ethylene diamine triacetic acid	20	85	—	—	85	—	—	107
Disodium salt of ethylene diamine tetra-acetic acid	15		55	—	100	—	120	—

From Table I which shows tin thickness in millionths of an inch, it can be seen that as the potassium hydroxide content increases from 2 to 12 g/l, the thickness of tin plated on aluminium undesirably increases 147 millionths from 92 to 239, a factor of 2.6, when the technique of this invention is not employed. The practice of this invention using e.g. trisodium salt of N-hydroxyethyl ethylene diamine triacetic acid reduces this undesirable increase in thickness to 22 millionths from 85 to 107, which represents an increase by a factor of 1.3 only.

#### EXAMPLE 2.

In this Example, which is typical of prior art practice, a bath was made up containing 70 g/l of potassium stannate and 4.0 g/l of potassium hydroxide by dissolving first the potassium hydroxide and then the potassium stannate. The bath was analyzed for free potassium hydroxide, and brought to 60° C.

Three pieces of D-132 aluminium 3×6×1/4" were degreased in trichloroethylene vapour, dipped for 30 seconds in a solution of 30 g/l of trisodium phosphate and

30 g/l of sodium carbonate at 60° C., rinsed in cold water, dipped for 30 seconds in a mixture of one part of concentrated nitric acid and 3 parts of water, rinsed in cold water, and immersed in two litres of the stanante solution for 4 minutes to deposit a layer of tin. The aluminium parts were then withdrawn, rinsed, and the tin deposit stripped from the aluminium parts by immersing for one minute in the nitric acid solution, and rinsing under a stream of cold water. The parts were then ready for the second dip in the stannate solution. A series of 10 successive dips and strippings is designated as a cycle in the Table below. At the end of each cycle, the bath was analyzed for free hydroxide and tin, and the tin content brought up to 28 g/l by addition of potassium stannate. At the beginning and end of each cycle, the thickness of the immersion coating was determined by means of difference in weight on a disc as described in Example 1.

The surface area plated during one cycle was 15 square feet per gallon of plating solution. The results are given in Table II.

TABLE II

Cycle	Start of Cycle		End of Cycle	
	Thickness of plate $10^{-3}$ inches	KOH g/l	Thickness of plate $10^{-3}$ inches	KOH g/l
1	84	3.1	127	4.85
2	95	4.85	157	4.90
3	134	4.90	140	4.90
4	127	4.90	167	—
5	136	—	170	8.5
6	224	8.5	186	9.8

5 The appearance of the tin deposit became streaky and gray and generally unsatisfactory after the fourth cycle, indicating an undesirably high hydroxide content. In order to maintain a satisfactory quality, neutralization would have been necessary after the fourth cycle. After the sixth cycle, the bath was filtered, the recovered sludge dried at 100° C. overnight and weighed. The weight of the dried sludge was 43.2 g.

## EXAMPLE 3.

15 Mixtures of potassium stannate and the disodium salt of ethylene diamine tetraacetic acid were made up. Mixture A contained

87.5% potassium stannate and 12.5% of the disodium salt of ethylene diamine tetraacetic acid. Mixture B contained 95% potassium stannate and 5% of the said disodium salt.

A bath was made up by dissolving 80 g/l of Mixture A and 3.2 g/l of potassium hydroxide in two liters of water. Again a test was conducted using a technique identical to that of Example 2, with the exception that the replenishment of the tin content of the bath after each cycle was accomplished by adding the appropriate quantity of Mixture B instead of potassium stannate. The results are given in Table III.

TABLE III

Cycle	Start of Cycle		End of Cycle	
	Thickness of Plate $10^{-3}$ inches	KOH g/l	Thickness of Plate $10^{-3}$ inches	KOH g/l
1	58	3.2	79	3.5
2	57	3.54	102	2.6
3	59	2.65	89	2.6
4	60	2.59	77	—
5	93	—	80	—
6	86	—	97	—
7	75	—	104	—
8	78	—	102	—

The quality of the deposit was good during the entire test with no streaking. This shows that the free potassium hydroxide content was constant during the test and even after eight cycles no need for neutralization existed. The sludge recovered from this bath was negligible.

Thus, it can be noted that a much smaller change in the thickness of the plate over the course of a cycle was obtained than was the case in Example 2. Neutralization was not needed to control the hydroxide and the sludging was substantially eliminated.

The above Examples show that the additives used in this invention are capable of permitting attainment of uniform and satisfactory tin immersion deposits on aluminium over wide ranges of caustic concentration in the solution. This benefit minimizes the need for acid additions to neutralize free hydroxide. In life tests the baths could be used at least 50% longer than the control solutions without addition of acid. The amount of sludge was considerably less for the baths containing the compositions of this invention.

It is a particular advantage of this invention that it permits operation of tin plating baths under conditions such that the thickness of the deposited tin plate is much more independent of the free alkali content of the bath than has been the case with prior art baths. It is another advantage of the process of this invention that it minimizes or eliminates the need for addition to the bath of acid to neutralize the hydroxide formed.

It appears that in tin plating baths, Reaction (I) *supra* may occur together with Reaction (III) below, the latter acting to neutralize the excess hydroxide generated in Reaction (I):



If the bath initially contained a low free alkali content, Reaction (I) may produce more alkali than is consumed by Reaction (III); in a bath with an initially high alkali content, Reaction (III) may consume more alkali than is produced by Reaction (I). In either case, the bath may reach an equilibrium at an intermediate level due to these reactions which may occur at the surface of the aluminium. The additives used in this invention allow the production of a satisfactory tin deposit even in the presence of an excess of hydroxide and thus provides a bath which is operable over a wide range of conditions.

After the bath has been operating for a considerable period of time, the aluminate produced by Reactions (I) and (III), which may be distributed throughout the bath, may react with water to produce sodium hydroxide and sludge in accordance with Reaction (IV):



It is believed that the presence in the bath of the compounds of this invention may reduce this reaction and thereby minimize the formation of hydroxide, and sludge including aluminium hydroxide.

#### WHAT WE CLAIM IS:—

1. A method of treating aluminium to form a surface layer of tin thereon which comprises immersing the aluminium in an aqueous bath comprising a nitrogen-containing Jongkind-chelating agent and sodium stannate or potassium stannate, maintaining the aluminium in the bath for time sufficient to deposit a surface layer of tin thereon, and withdrawing the aluminium from the bath.

2. The method of treating aluminium to form a surface layer of tin thereon as claimed in Claim 1, wherein the said Jongkind-chelating agent is chosen from ethylene diamine tetraacetic acid, N,N-dihydroxy ethyl glycine, and water soluble salts thereof.

3. The method of treating aluminium to form a surface layer of tin thereon as claimed in Claim 1, wherein the said agent is the disodium salt of ethylene diamine tetraacetic acid.

4. The method of treating aluminium to form a surface layer of tin thereon as claimed in any preceding claim, wherein the said agent is present in an amount of 0.01—0.25 mole per liter.

5. The method of treating aluminium to form a surface layer of tin thereon as claimed in any preceding claim, wherein the stannate is present in an amount of 15 grams per litre to saturation.

6. A method of treating aluminium to form a surface layer of tin thereon which comprises immersing the aluminium in an aqueous bath containing potassium stannate and the disodium salt of ethylene diamine tetraacetic acid, maintaining the aluminium in the bath for 30 seconds—6 minutes during which time a surface layer of tin is deposited thereon, and withdrawing the aluminium from the bath.

7. An alkaline aqueous immersion tinning bath comprising a nitrogen-containing Jongkind-chelating agent, and sodium stannate or potassium stannate.

8. An alkaline aqueous immersion tinning bath comprising (1) a nitrogen-containing Jongkind-chelating agent chosen from the ethylene diamine tetraacetic acid, N,N-dihydroxy ethyl glycine, and water soluble salts thereof, and (2) sodium stannate or potassium stannate.

9. An alkaline aqueous immersion tinning bath comprising the disodium salt of ethylene diamine tetraacetic acid, and sodium stannate or potassium stannate.

10. A composition comprising a compound containing (1) a nitrogen-containing Jongkind-

chelating agent, and (2) a sodium stannate or potassium stannate.

- 5 11. A composition comprising (1) a compound chosen from ethylene diamine tetraacetic acid, N,N-dihydroxy ethyl glycine, and water soluble salts thereof, and (2) sodium stannate or potassium stannate.

- 10 12. A composition comprising a sodium stannate or potassium stannate and 1%—20% by weight of the total of a compound chosen from ethylene diamine tetraacetic acid, N,N-dihydroxy ethyl glycine, and water soluble salts thereof.

- 15 13. A composition comprising 80%—99% potassium stannate and 1%—20% disodium salt of ethylene diamine tetraacetic acid.

14. A composition comprising 98% potas-

sium stannate and 2% disodium salt of ethylene diamine tetraacetic acid.

15. A method according to any one of Claims 1 to 6 substantially as herein described. 20

16. Aluminium plated with tin by the method claimed in any one of Claims 1 to 6 or Claim 15.

17. An alkaline immersion tinning bath according to any one of Claims 7 to 9 substantially as herein described. 25

18. A composition according to any one of Claims 10 to 14 substantially as herein described. 30

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